

LA-UR-21-28257

Approved for public release; distribution is unlimited.

Title: High Dose and Dose Rate ^{60}Co Gamma-Irradiation of High-Density Polyethylene

Author(s): Safarik, Douglas Joseph
Cummins, Dustin Ray
Capelli, Deanna
Honnell, Peggy Diana (Diana)
Bernal, John Edmund
Wasiolek, Maryla
Hanson, Donald

Intended for: Report

Issued: 2021-08-18

Disclaimer:

Los Alamos National Laboratory, an affirmative action/equal opportunity employer, is operated by Triad National Security, LLC for the National Nuclear Security Administration of U.S. Department of Energy under contract 89233218CNA000001. By approving this article, the publisher recognizes that the U.S. Government retains nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or to allow others to do so, for U.S. Government purposes. Los Alamos National Laboratory requests that the publisher identify this article as work performed under the auspices of the U.S. Department of Energy. Los Alamos National Laboratory strongly supports academic freedom and a researcher's right to publish; as an institution, however, the Laboratory does not endorse the viewpoint of a publication or guarantee its technical correctness.

High Dose and Dose Rate ^{60}Co γ -Irradiation of High-Density Polyethylene

D. J. Safarik,* D. R. Cummins, D. Capelli, P. D. Honnell, and J. E. Bernal

Sigma Division, Los Alamos National Laboratory, Los Alamos, NM 87544

M. Wasiolek and D. Hanson

Gamma Irradiation Facility, Sandia National Laboratory, Albuquerque, NM 87123

(Dated: August 16, 2021)

Abstract

We have irradiated high-density polyethylene ribbons and cylinders to ~ 200 kGy at a dose rate of ~ 5 kGy day $^{-1}$, using a ^{60}Co source. The radiolytically-generated gas consists almost entirely of H_2 . Based on the time- and dose-dependence of the outgassing, we have determined the radiation-chemical yield for the evolved H_2 , as well as the diffusion coefficient of H_2 in HDPE. We find that the evolved gas yield G_{evolved} depends on the interplay of sample geometry, experimental timescale, and the diffusion coefficient of H_2 in HDPE. When these factors facilitate completion of diffusion prior to gas quantification, such as for sub-mm-thickness ribbons, we measure a time- and dose-invariant value of $G_{\text{evolved}} = 0.0076 \text{ cm}^3 \text{ std. H}_2 \text{ J}^{-1}$ that is in agreement with literature reports. When sample geometry and experiment timescale do not permit completion of diffusion, we measure a time- and dose-dependent value of G_{evolved} . We have developed a model for the transient outgassing behavior of the cylinders, and fitted it to the experimental data. Based on these fits, we estimate a room-temperature diffusivity of $D_{\text{H}_2/\text{HDPE}} \approx 1.67 \pm 0.12 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ for H_2 in HDPE, in good agreement with literature values. At present, the effects of dose rate and γ -photon energy on HDPE gas yield are not known and require further investigation.

I. INTRODUCTION

Space, nuclear reactor, and national-security-related applications often demand that materials function at extremes of temperature, mechanical stress, chemical attack, radiation exposure, or some combination thereof. Reliable prediction of material performance in such environments, particularly over long timescales relevant to desired lifetimes, requires at least some understanding of the chemical and physical processes responsible for performance degradation. Usually this is accomplished via short- and long-term “aging” experiments, where a material is subjected to relevant extreme conditions for times ranging from days to years, and pertinent properties are characterized and quantified via in-situ monitoring and/or post-mortem analysis. It is often advantageous to incorporate the understanding and data acquired from such experiments into models or simulations that capture the physics and chemistry of degradation. The predictive power of such models can then be tested against experiments performed at somewhat different extreme conditions.

* dsafarik@lanl.gov

At Los Alamos, a particular concern associated with extreme conditions is the radiation-induced generation of gases, for example H_2 , CH_4 , CO_2 , etc. More specifically, we are interested in the identity and quantity of gases generated, as well as the radiation-chemical mechanism(s) by which they form. In the literature, identification and quantification of radiolytically-generated evolved gases has been accomplished via two methods: (1) Dynamic techniques where the outgas is continuously removed from the headspace by means of a sweep gas or a vacuum system, and this effluent is routed through a mass spectrometer or gas chromatograph/mass spectrometer combination to identify and quantify the gases generated;¹⁻⁷ and (2) Static methods where the outgas accumulates in the closed headspace of the hermetically sealed irradiation vessel, and the gas is quantified and chemically analyzed after the irradiation is complete.^{2,8-13}

The dynamic method is most compatible with irradiation experiments of short duration and where space constraints permit proximate installation of the necessary gas flow or vacuum system, plus associated chemical analysis instrumentation. Neither of these conditions are satisfied for our laboratory “radiation aging” experiments. Indeed, our experiments usually require 1-5 years of low-dose-rate γ -irradiation to accurately simulate the service environment that is typical of our material applications. Due to the long experimental timescales, together with space constraints imposed by our need to radiation-age at isothermal conditions inside environmental chambers, we have found the dynamic gas quantification method difficult to implement. Therefore, our standard practice has been to use the static gas accumulation method, with real-time, in-situ quantification of evolved gas by means of continuous pressure-volume-temperature measurements, followed by post-mortem chemical analysis.

There are at least two potential problems associated with the gas accumulation technique. First, the evolved gas is irradiated for long periods of time and could potentially undergo radiolysis and/or participate in gas-gas or gas-solid chemical reactions, thereby complicating data analysis and interpretation. Second, some quantity of the generated gas will remain physically dissolved in the material due to gas-solid partitioning effects (i.e., Henry’s Law). If the solubility is large, the evolved gas quantity will not accurately represent the generated gas quantity. For these reasons, we are motivated to evaluate the accuracy of the gas accumulation method that we use in our laboratory.

In this report we quantify the evolved gas and radiation-chemical evolved gas yield,

$G_{evolved}$, for high-density polyethylene (HDPE) using a gas accumulation method. Our results compare favorably to literature values of $G_{evolved}$ measured using both static^{9,10} and dynamic^{1,5,6} techniques. This suggests that the gas accumulation method used in our laboratory is indeed a viable approach to accurately quantify gas evolution from solids undergoing irradiation, at least when the radiolytically-generated gas consists mainly of “permanent” gases such as H₂, CH₄, N₂, CO₂, etc., when the accumulated gas pressure is low (i.e., < 1 atmosphere), and when the physical solubility of the gases in the solid is small.

II. EXPERIMENTAL METHODS

Stock HDPE rods, 200 mm long \times 50 mm diameter, were obtained from Goodfellow Corporation (Part No. ET327950) and machined into either 6.1 cm long \times 3.6 cm diameter cylinders or \sim 2.5 mm wide \times \sim 0.25 mm thick ribbons. Typical sample masses were 55 g for cylinders and 20 g for ribbons. Fig. 1 shows photos of representative specimens before irradiation. Prior to machining the stock HDPE into these shapes, the cutting tools were carefully cleaned by sonicating in a detergent bath and then rinsing in ethanol to minimize possible contamination of the HDPE from machine oils. After machining, the HDPE specimens were cleaned via wiping with or soaking in ethanol (in the case of cylinders and ribbons, respectively). The macroscopic specific surface area of the cylinders and ribbons, calculated from sample geometry, were 1.53 cm² g⁻¹ and \sim 100 g cm² g⁻¹, respectively. As a result, we expected that escape of radiolytically-generated gases would be much faster from the ribbon samples than the cylindrical monoliths. This is indeed what we observed, as discussed later.

During our irradiation experiments, the HDPE samples were contained in custom-built, ultra-high-vacuum-compatible aging assemblies. Figure 2(a) shows a schematic of the assembly, and Fig. 2(b) shows a photograph. The sample chamber section of the assembly is a closed-ended half-nipple that is constructed from 6061 aluminum. The upper flange of this aluminum can is explosion-bonded to a 2.75” stainless steel conflat flange. Nominal internal dimensions of the sample chamber are 7.6 cm tall \times 3.8 cm diameter, with a volume of approximately 87 cm³. We should note that aluminum was selected as the chamber material for two reasons: (1) Hydrogen has a very low solubility in Al, thus outgassing or absorption of hydrogen by the chamber walls is minimized, especially compared to stainless steel; (2)

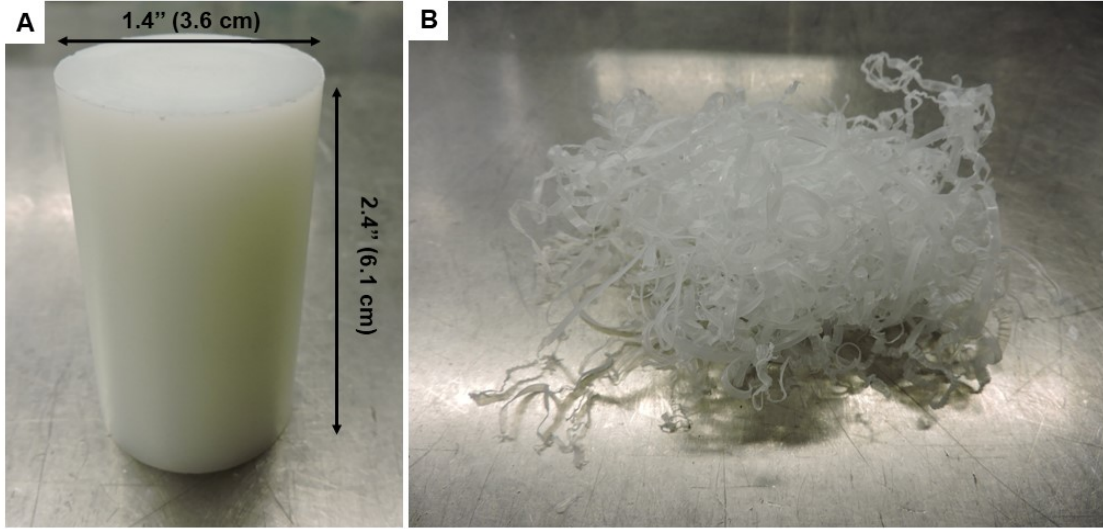


FIG. 1. Photographs of (a) HDPE cylinder and (b) HDPE ribbon turnings prior to ^{60}Co irradiation.

Aluminum, being a low-Z metal, is significantly more transparent to photons than stainless.

The 2.75" conflat-flanged lid is also constructed from stainless steel and is fitted with a 1/4" stainless female VCR fitting. As shown in Fig. 2, this fitting is connected to a manifold containing a Baratron pressure manometer (MKS Instruments, Baratron model 121A), 1-inch diameter pressure relief rupture disk with nominal maximum burst pressure 25 psig (Scientific Vacuum Sales, part No. 6-103902), metal-sealed VCR-fitting valves for gas management (Swagelok part no. SS-4H-VCR and SS-4H-V51), and a 25 cm³ stainless steel gas bottle with integral 4H metal seal valve (Swagelok part no. SS-4H-W72) for collection of headspace gas samples. After thorough leak-testing using He gas and a mass spectrometer, each vessel was vacuum-baked at 150°C for ~3 days until the pressure was in the 10⁻⁷ torr range. The purpose was to reduce the quantity of water adsorbed to the surfaces of the assembly.

Cylinders and ribbons were loaded into the baked assemblies inside of a nitrogen-atmosphere glovebox. Following loading, the assemblies were once again evacuated to the 10⁻⁷ torr range and then He-leak-tested a final time.

We irradiated six HDPE samples (three cylinders and three ribbons) at room temperature (uncontrolled) using a ^{60}Co source in Cell #2 at the Sandia National Laboratories Gamma Irradiation Facility (GIF). ^{60}Co produces γ -photons with energies 1.173 and 1.332 MeV, and has a half-life of 5.27 years. To achieve approximately the same absorbed dose for

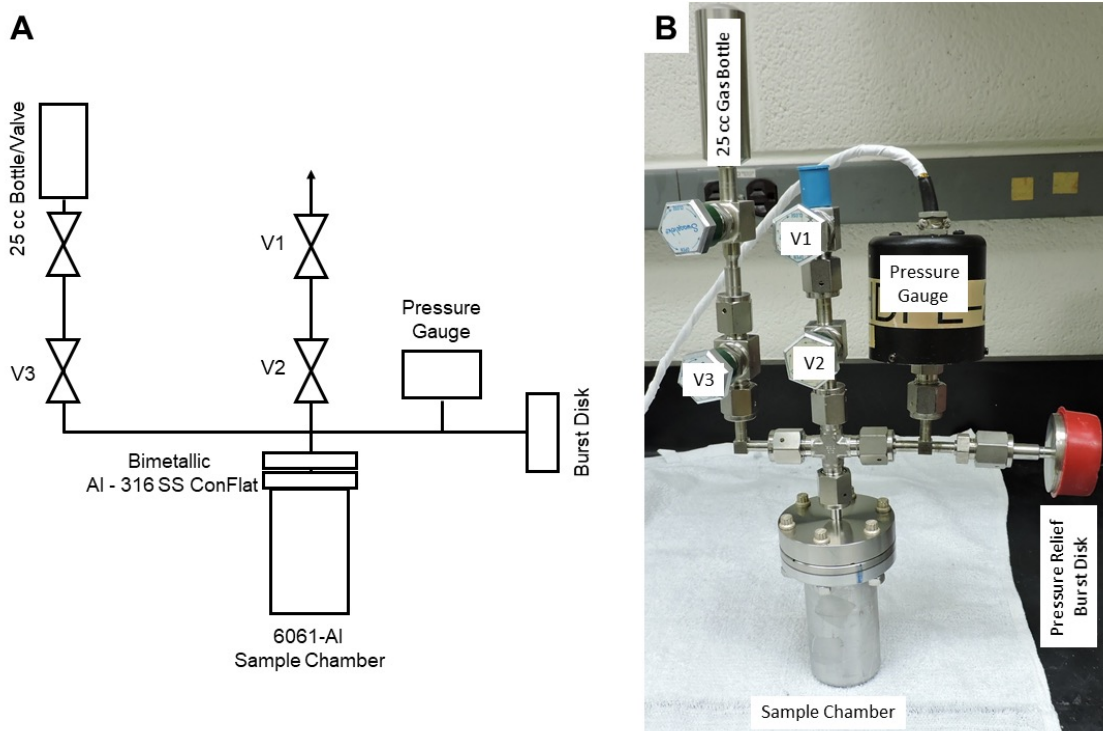


FIG. 2. Schematic (a) and photograph (b) of radiation-aging assembly. The assembly consists of an aluminum sample chamber with a 2.75" stainless steel conflat flange (explosion-bonded aluminum-stainless interface), plus a pressure manometer, pressure relief burst disk, gas sampling bottle, and associated valving and tubulation for gas management.

each sample, the irradiation vessels were arranged in a semicircular pattern with each at a distance of 2.4 m (94 inches) from the ^{60}Co source. Figures 3(a) and (b) show a schematic and a photograph, respectively, of the vessel layout in GIF Cell #2. All six HDPE samples were irradiated for 40.6 days at a dose rate of 5.9 rad s^{-1} (5090 Gy day^{-1}), for a total absorbed dose of 20.7 Mrad (0.207 MGy). Dose information was determined from ion chamber measurements performed at the start of the irradiation experiments. For these, we briefly added a seventh aluminum can, containing an ion chamber, to the sample array array in Fig. 3. This seventh can is not shown in the figure.

During irradiation, we continuously monitored the pressure and temperature for each sample using the Baratron manometer (see Fig. 2) and a thermocouple. Data were collected using CompactRIO (cRIO) chassis and modules from National Instruments. This data acquisition (DAQ) system was placed outside of Cell #2 to prevent damage from the intense radiation. Signal cables from the DAQ system to the Baratron manometers and thermocou-

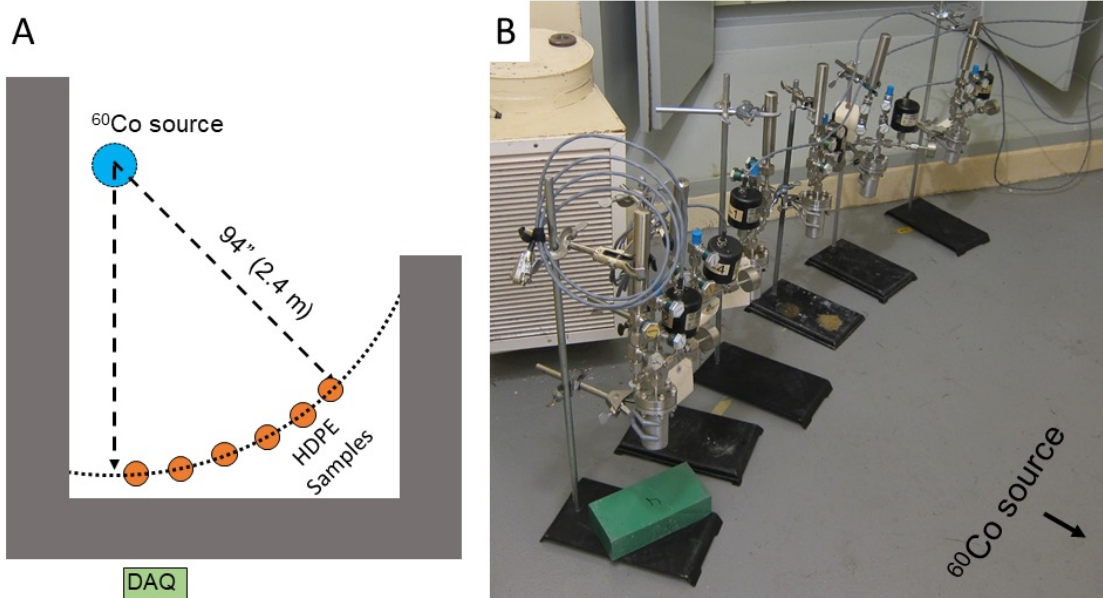


FIG. 3. Schematic (a) and photograph (b) of the HDPE sample layout in Cell #2 at the Sandia National Laboratory GIF. Here we do not show the seventh aluminum sample chamber, containing an ion chamber, that was briefly added to the sample array to measure the absorbed dose rate.

ples were routed through the 7-foot-thick cell walls via small portholes with tortuous paths. The pressure and temperature data, together with measurements of the headspace volume of each irradiation vessel, enabled us to use the ideal gas law to compute the total quantity of gas evolved (from all species) as a function of time and hence absorbed dose. Following irradiation, samples of the evolved gas were collected in the gas bottles shown in Fig. 2, and were analyzed via gas chromatography/mass spectrometry (GC/MS).

III. RESULTS

Figure 4 panels (a) and (b) show the total quantity of gas evolved from two solid HDPE cylinders and two HDPE ribbons as a function of irradiation time (panel (a)) and absorbed dose (panel (b)) during irradiation at $5,090 \text{ Gy day}^{-1}$. (Data for the third cylinder and ribbon are similar.) Note that the units of dose in panel (b) are kGy; the dose absorbed during the experiment was $>200,000 \text{ Gy}$. This high dose was used to generate an adequate quantity of gas for reliable determination of the radiation-chemical evolved gas yields, G_{evolved} .

As shown in both panels, for HDPE ribbons the gas quantity evolved increases linearly

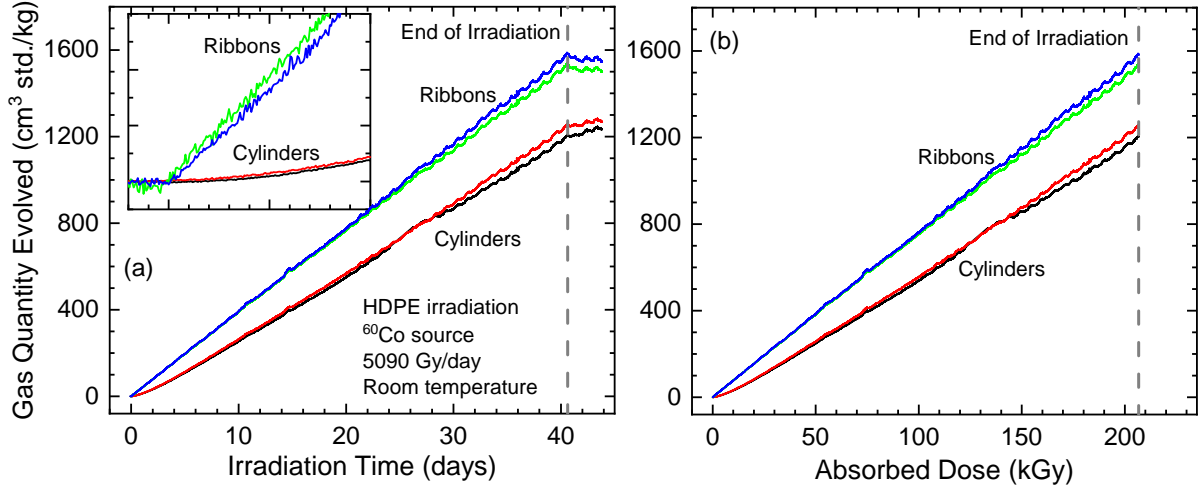


FIG. 4. (a) Time and (b) absorbed dose dependence of the total quantity of gas evolved from HDPE cylinders and ribbons during room-temperature ^{60}Co irradiation (1.173 and 1.332 MeV γ -rays) at the Sandia GIF. The inset to panel (a) shows a magnification of the outgassing traces from -0.02 days (i.e., 70 minutes before the irradiation began) to 0.1 days. Notice that for the ribbons, the outgassing traces are linear from the moment that the irradiation begins, whereas for the cylinders there is initially some curvature to the traces before linearity is achieved.

with time and dose during exposure to the 1.173 and 1.332 MeV γ -photons. The linearity begins immediately with the start of irradiation. This is more evident in the Fig. 4(a) inset, which shows a magnification of the abscissa from -0.02 days (i.e., 70 minutes before the irradiation started) to 0.1 days. For the HDPE cylinders, we observe some curvature to the evolved gas traces during the first ~ 10 days, after which the traces become essentially linear. As discussed below, we hypothesize that this transient behavior is associated with the diffusion of radiolytically-generated gas out of the monolithic samples. This hypothesis is also supported by the outgassing behavior upon suddenly stopping the irradiation, at 40.6 days and 207 kGy dose. Notice that for the ribbons, the outgassing abruptly ceases upon removal of the ionizing radiation (panel (a)). In contrast, for the cylinders the outgassing continues for at least 3 days (the limit of our measurements), albeit at a decreased rate. Presumably this continued outgassing is associated with the continued diffusion of gas out of the monoliths during the post-irradiation period.

Figure 5 shows the radiation-chemical evolved gas yield, G_{evolved} , as a function of (a) irradiation time and (b) dose for the cylindrical and ribbon HDPE samples discussed in

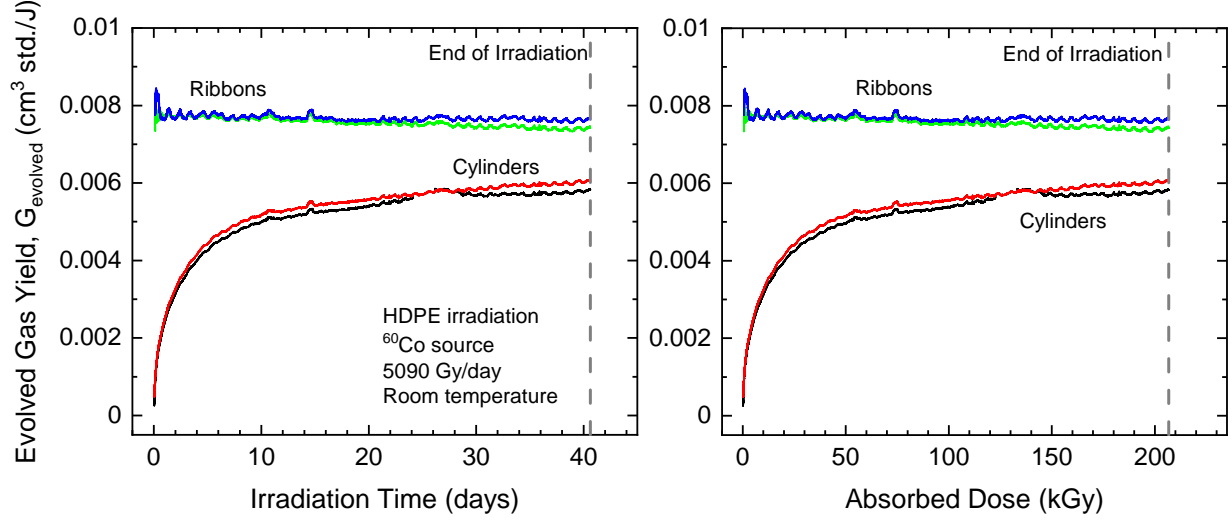


FIG. 5. Radiation-chemical evolved gas yield, $G_{evolved}$, as a function of (a) irradiation time and (b) absorbed dose during room-temperature ^{60}Co irradiation (1.173 and 1.332 MeV γ -rays) of HDPE cylinders and ribbons at the Sandia GIF. Notice that the ribbon yields are virtually independent of dose and time, with $G_{evolved} \approx 0.00760 \text{ cm}^3 \text{ J}^{-1}$. In contrast, the yield from the cylinders increases with irradiation time and dose. This observation reflects the transient outgassing behavior seen for the cylinders in Fig. 4, for irradiation times of <10 days (50 kGy). Most likely, this is associated with the specimen size together with the finite rate of gas diffusion in HDPE.

Fig. 4. Here, we calculate $G_{evolved}$ as the *average* slope of the evolved gas quantity vs. dose curves at a particular dose, i.e., the total quantity evolved up to a particular dose or time divided by that absorbed dose. Alternatively, we could have also computed $G_{evolved}$ as the *instantaneous* slope of the gas evolved vs. dose curve at a particular dose. For the present work, we adopted the former approach because it is consistent with literature reports of $G_{evolved}$ for HDPE.^{1,6,9,10,12}

As seen in Fig. 5, $G_{evolved}$ for the ribbons is virtually independent of time and absorbed dose, although close inspection suggests a very gradual decrease with increasing time and dose. For these two ribbons the average yields during the 40.6-day period of active irradiation were $G_{evolved} = 0.00756 \pm 0.00011$ and $0.00768 \pm 0.00008 \text{ cm}^3 \text{ std. J}^{-1}$. Our values compare favorably with those reported in the literature using both gas accumulation^{9,10} and dynamic outgassing^{1,6,12} techniques. These literature values range from 0.0065 to 0.0088 $\text{cm}^3 \text{ std. J}^{-1}$, with most measurements between 0.007 and 0.0077 $\text{cm}^3 \text{ std. J}^{-1}$. We should note that these authors studied powders,⁹ films,^{1,5,6,10} and thin sheets^{5,6} having specific surface areas

comparable to the specimens used in our studies. Chang and LaVerne⁵ studied in detail the effect of sample specific surface area on $G_{evolved}$, and found that when the surface area of their thin-sheet specimens exceeded $\sim 50 \text{ cm}^2 \text{ g}^{-1}$, diffusion of radiolytically-generated gas out of the sheets was completed on the timescale of their experiments, and the radiation chemical yield plateaued at $G_{evolved} = 3.1 \text{ molecules} / 100 \text{ eV}$. This is equivalent to $0.00720 \text{ cm}^3 \text{ std. J}^{-1}$, which is approximately 5% smaller than the values we measure but is consistent with the above-cited literature. As discussed further below, for accurate determination of $G_{evolved}$ it is important that the sample geometry, as characterized by the specific surface area, together with the experimental timescale during and after irradiation, be such that the radiolytically generated gases have sufficient time to diffuse out of the specimen. Evidently, this was the case for the studies we cite here. We should note that surface area corresponding to the $G_{evolved}$ plateau reported by Chang and LaVerne,⁵ $\sim 50 \text{ cm}^2 \text{ g}^{-1}$, is arbitrary in the sense that it corresponds only to the particular experimental timescale used by these authors.

In contrast to the ribbons, the value of $G_{evolved}$ for the cylinders gradually increases as irradiation time and hence absorbed dose increase. This is a reflection of the non-linear time- and dose-dependence of the evolved gas trace that we observe in Fig. 4 during the first 10 days (50 kGy) of irradiation. At the conclusion of the 40.6-day irradiation, the yield from our cylinders is $G_{evolved} \approx 0.0059 \text{ cm}^3 \text{ J}^{-1}$. This value is much larger than the $\approx 0.00040 \text{ cm}^3 \text{ J}^{-1}$ yield that we deduced via interpolation of Chang and LaVerne's $G_{evolved}$ vs. specific surface area data for the specific surface area of our cylinders, $1.53 \text{ cm}^2 \text{ g}^{-1}$.⁵ We hypothesize that this discrepancy is associated with a relatively longer experimental timescale for our experiments than Chang and LaVerne's, which enabled additional diffusion of gas out of our samples.

Immediately after completion of the irradiation, we collected samples of the evolved gas and analyzed them using gas chromatography/mass spectrometry (GC/MS). We detected only five gases in the headspace above the samples: H_2 , CH_4 , N_2 , O_2 , and CO . Most likely, trace quantities of H_2O are also present, but below the detection limit of our GC/MS system. As shown in Table I, H_2 was by far the main constituent of the gas. This result is consistent with literature reports.^{1,5,6,9,10,14,15} Nitrogen, O_2 , CH_4 , and CO were present in small amounts. We suspect that O_2 and at least some of the N_2 originated from a small leak in the sample loop of the gas chromatograph, whose existence became evident after this analysis. This may be particularly true for ribbon samples #1 and #2. Another possible

TABLE I. Headspace gas composition and gas quantities evolved from HDPE cylinders and ribbons during ^{60}Co irradiation to 207 kGy at the Sandia GIF.

Gas)	Cylinder 1	Cylinder 2	Cylinder 3	Ribbon 1	Ribbon 2	Ribbon 3
H ₂ (mol %)	97.89	98.86	98.20	96.65	95.67	98.82
CH ₄ (mol %)	0.07	0.07	0.09	0.61	0.59	0.61
N ₂ (mol %)	1.63	0.88	1.39	0.68	0.94	0.21
O ₂ (mol %)	0.33	0.13	0.26	1.83	2.55	0.10
CO (mol %)	0.07	0.07	0.06	0.23	0.25	0.26
H ₂ (cm ³ kg ⁻¹)	1208.8	1215.2	1248.1	1476.6	1433.6	1530.4
CH ₄ (cm ³ kg ⁻¹)	0.9	0.8	1.2	9.3	8.9	9.5
N ₂ (cm ³ kg ⁻¹)	20.2	10.8	17.7	10.4	14.1	3.3
O ₂ (cm ³ kg ⁻¹)	4.1	1.5	3.3	28.0	38.2	1.6
CO (cm ³ kg ⁻¹)	0.9	0.8	0.8	3.5	3.8	4.0

source of N₂ is the dissolution of nitrogen in the HDPE during handling and storage of the samples in our N₂-atmosphere glovebox.

IV. DISCUSSION

As noted in Section III, using a gas accumulation technique we measure yield values of $G_{\text{evolved}} \approx 0.0076 \text{ cm}^3 \text{ std. J}^{-1}$ for thin HDPE ribbons with specific surface areas of $\sim 100 \text{ cm}^2 \text{ g}^{-1}$. This value compares favorably with those reported in the literature, as measured for powders,⁹ films,^{1,5,6,10} and thin sheets^{5,6} using gas accumulation^{9,10} and dynamic outgassing^{1,6,12} techniques. Literature values range from 0.0065 to 0.0088 cm³ std. J⁻¹, with most measurements clustered between 0.007 and 0.0077 cm³ std. J⁻¹. We should stress that to obtain reliable measurements of G_{evolved} , the experimental timescale must be sufficiently long that diffusion of radiolytically-generated gases out of the HDPE sample is substantially complete. This was demonstrated by Chang and LaVerne⁵, who showed that when this condition is met the value of G_{evolved} plateaus at $\approx 3.1 \text{ molecules} / 100 \text{ eV}$ (0.00720 cm³ std. J⁻¹). If the combination of specimen size and experimental timescale do

not allow for substantial completion of diffusion, then lower values of $G_{evolved}$ are measured because a fraction of the radiolytically-generated gas has not yet emerged from the HDPE.

The agreement of our $G_{evolved}$ values with literature values suggests that our implementation of the gas accumulation method gives accurate measurements of the radiation-chemical evolved gas yield. The gas accumulation technique is likely most reliable when (1) the headspace gas consists mainly of small molecules that are characterized by high ionization energies, and (2) the headspace overpressure is low, i.e., less than approximately one atmosphere. Both of these factors reduce the probability of radiolytically-driven gas-gas and gas-solid reactions.

A third requirement for accuracy of the method is that the physical solubility of the primary evolved gas(es) in the solid is(are) low. As shown in Table I, the main gaseous product of HDPE radiolysis is H_2 . The physical solubility of H_2 in HDPE obeys Henry's Law, $C_{H_2} = S_{H_2}P_{H_2}$, where C_{H_2} is the dissolved gas concentration, S_{H_2} the Henry's Law (solubility) coefficient, and P_{H_2} the H_2 partial pressure.¹⁶ At 20°C, $S_{H_2} = 4.3 \text{ mol } H_2 \text{ m}^{-3} \text{ MPa}^{-1}$,¹⁶ or $10 \text{ cm}^3 \text{ std. } H_2 \text{ kg}^{-1} \text{ atmosphere}^{-1}$. At the conclusion of these irradiation experiments, the headspace pressures were ~ 250 torr and ~ 850 torr, respectively, for the ribbons and cylinders. This corresponds to approximately 3 and $11 \text{ cm}^3 \text{ std. } H_2 \text{ kg}^{-1}$ physically dissolved in the HDPE, which represents just $\sim 0.2\%$ and $\sim 1\%$ of the total quantity evolved. We concluded that the quantity of H_2 *physically* dissolved in the HDPE is indeed negligible.

Here we should distinguish between H_2 that is *physically dissolved* in the solid and H_2 that is *trapped at defect sites*. Such defects might be created by interaction of the energetic γ -photons with the HDPE. In the case of physical dissolution, H_2 is readily removed by evacuation of the headspace above the HDPE specimen. By contrast, trapped H_2 may be difficult or impossible to remove even after heating for extended times in vacuum. In the present work we have not quantified the trapped H_2 .

In the literature work cited in this report, the absorbed dose rates range from 26 to 402 kGy day^{-1} .^{5,6,9,10} For our experiments the dose rate was somewhat lower at $5.09 \text{ kGy day}^{-1}$. Based on the available data, it appears that the value of $G_{evolved}$ is relatively constant at 0.007 to $0.0077 \text{ cm}^3 \text{ std. J}^{-1}$ over this 80-fold range of dose rates. *However, we should point out that these dose rates are 6-8 orders of magnitude larger than the $\sim 1\text{-}100 \text{ Gy year}^{-1}$ ($0.003\text{-}0.3 \text{ Gy day}^{-1}$) that might be more characteristic of applications relevant to LANL.* We stress this point because, depending on the details of the radical chain reaction mechanism,

the G value can show a strong dependence on the dose rate.¹⁷ For example, if the kinetics of the radical chain termination reaction(s) is(are) second-order in the concentration of the radicals that propagate the chain, then a simple analysis predicts that $G \propto R_m^{-1/2}$, where R_m is the absorbed dose rate.¹⁷ In other words, *as the dose rate decreases, the value of G increases*. We have indeed observed an increase in $G_{evolved}$ with decreasing R_m for other materials that are of interest to LANL. Our point is that because the presently available $G_{evolved}$ data for HDPE were measured at exceedingly large dose rates, we do not know whether more realistic rates in the $\sim 1\text{-}100\text{ Gy year}^{-1}$ range will result in $G_{evolved}$ values significantly different from the $0.007\text{ to }0.0077\text{ cm}^3\text{ std. J}^{-1}$ discussed here. *To answer this question, we must perform experiments at relevant, much lower dose rates.*

We also note that in all literature studies reference here,^{1,2,4-6,9,10,14} the γ -irradiation was accomplished using ^{60}Co sources (1.173 and 1.332 MeV), just as in our experiments. We are presently not aware of any work using lower-energy photon sources, such as ^{137}Cs (662 keV) or ^{241}Am (59.6 keV). *Therefore, at this time the effect of γ -photon energy on the radiation-aging and outgassing behavior of HDPE is not known.*

In contrast to the HDPE ribbons, where the value of $G_{evolved}$ is essentially time- and dose-invariant (see Fig. 5), for the HDPE cylinders the yield increases throughout the duration of the irradiation. At the conclusion of the experiment, the value was $\sim 0.0059\text{ cm}^3\text{ std. J}^{-1}$. Considering the upward trend in these data, it seems plausible that $G_{evolved}$ would eventually plateau at the same value we measure for the ribbons, $0.0076\text{ cm}^3\text{ std. J}^{-1}$, if we waited for diffusion of gas (H_2) out of the cylinders to be substantially complete. Extrapolation of the evolved gas vs. irradiation time data in Fig. 5(a) suggests that a waiting time of ~ 90 days following the end of irradiation would be required for $G_{evolved}$ to reach $0.0076\text{ cm}^3\text{ std. J}^{-1}$. Using the diffusivity of H_2 in Goodfellow HDPE measured by Change and LaVerne,^{5,6} $D_{\text{H}_2/\text{HDPE}} = 2.2 \times 10^{-6}\text{ cm}^2\text{ s}^{-1}$, we can estimate a characteristic time for the diffusion to be substantially complete for our $3.6\text{ cm diameter} \times 6.1\text{ cm tall}$ cylinders as $t_{Diff} \approx 5 L^2/D_{\text{H}_2/\text{HDPE}}$, where L is a characteristic length. Using the cylinder radius and half-height as the characteristic lengths, we estimate t_{Diff} to be in the range 80 to 250 days. This is in good agreement with the estimated 90-days of post irradiation time (130 days including irradiation time) needed for diffusion to be mostly complete. Based on this simple analysis, we tentatively conclude that the finite rate of diffusion, together with the cylinder size, is responsible for the time- and dose-dependence of $G_{evolved}$ observed in Fig. 5,

as well as the transient in the evolved gas quantity observed in Fig. 4 for irradiation times (doses) less than ~ 10 days (50 kGy).

In principle, proper analysis of the cylinder data in Fig. 4 should enable us to estimate the diffusion coefficient of radiolytically-generated H_2 within the HDPE. To proceed with such an analysis, we first need a model. Unfortunately, we were unable to locate an applicable “turnkey” model in the seminal monograph on diffusion by Crank.¹⁸ We therefore adopted a solution from “The Conduction of Heat in Solids” by Carslaw and Jaeger¹⁹ using appropriate analogies between heat and mass transport. We began with the solution for the steady-state temperature profile inside a finite cylinder ($0 \leq z \leq L$, $0 < r \leq a$) where heat is generated at a constant rate A_0 per unit volume. The temperature profile is given on page 223-224 in Carslaw and Jaeger,¹⁹

$$T(r, z) = \frac{A_0 z(L - z)}{2K} - \frac{4L^2 A_0}{K\pi^3} \sum_{n=0}^{\infty} \frac{I_0 \left[(2n+1) \frac{\pi r}{L} \right]}{(2n+1)^3 I_0 \left[(2n+1) \frac{\pi a}{L} \right]} \sin \left[(2n+1) \frac{\pi z}{L} \right], \quad (1)$$

where L is the length of the cylinder, a is the radius, K is the thermal conductivity, and I_0 is the modified Bessel function of the first kind. Using heat-mass transport analogies, we convert this equation into one that describes the steady-state *concentration* profile $c(r, z)$ inside a finite cylinder ($0 \leq z \leq L$, $0 < r \leq a$) in which *solute* is generated at a constant rate G_0 per unit volume,

$$c(r, z) = \frac{G_0 z(L - z)}{2D_{eff}} - \frac{4L^2 G_0}{D_{eff}\pi^3} \sum_{n=0}^{\infty} \frac{I_0 \left[(2n+1) \frac{\pi r}{L} \right]}{(2n+1)^3 I_0 \left[(2n+1) \frac{\pi a}{L} \right]} \sin \left[(2n+1) \frac{\pi z}{L} \right], \quad (2)$$

where D_{eff} is the effective diffusion coefficient of the solute in the cylinder.

At this steady-state condition, the quantity of solute (H_2 gas) retained inside the cylinder is

$$R_{SS} = \int_0^L \int_0^a 2\pi r c(r, z) dr dz. \quad (3)$$

The quantity of gas generated between time 0 and time t , assuming a temporally constant and spatially uniform generation rate per unit volume G_0 , is

$$G(t) = \pi a^2 L G_0 t. \quad (4)$$

Finally, the difference between the total quantity generated and that retained inside the

solid at steady state equals the gas quantity evolved at steady state,

$$Q(t) = G(t) - R_{ss} = \pi a^2 L G_0 t - \int_0^L \int_0^a 2\pi r \left[\frac{G_0 z(L-z)}{2D_{eff}} - \frac{4L^2 G_0}{D_{eff} \pi^3} \sum_{n=0}^{\infty} \frac{I_0 \left[(2n+1) \frac{\pi r}{L} \right]}{(2n+1)^3 I_0 \left[(2n+1) \frac{\pi a}{L} \right]} \sin \left[(2n+1) \frac{\pi z}{L} \right] \right] dr dz. \quad (5)$$

Integrating Eq.(5) gives

$$Q(t) = \pi a^2 L G_0 t - \frac{18.275 G_0}{D_{eff}}, \quad (6)$$

where we have substituted the dimensions of our HDPE cylinders ($a = 1.8$ cm, $L = 6.1$ cm) to facilitate the integration. This linear equation describes the quantity of gas evolved as a function of time after establishment of steady-state, i.e., for times (doses) greater than ~ 10 days (~ 50 kGy) in Fig. 4. Extrapolation of this line to the time axis (e.g., $Q(t) = 0$) yields an intercept t^* of

$$t^* = \frac{0.30186}{D_{eff}}, \quad (7)$$

where t^* and D_{eff} are in units of seconds and $\text{cm}^2 \text{s}^{-1}$, respectively. Thus by fitting a straight line to the cylinder data after steady-state outgassing is established, and determining the x-intercept of this line t^* , we can determine the diffusion coefficient of H_2 in HDPE,

$$D_{eff} = \frac{0.30186}{t^*}. \quad (8)$$

Figure 6 shows gas quantity evolved from two HDPE cylinders as a function of irradiation time, just as in Fig. 4(a). However, here we have also fitted straight (dashed) lines to the experimental data (solid curves) for irradiation times in the range 10 to 40 days, where the cylinder outgassing shows steady-state behavior. Extrapolation of these lines gives the values of the x-intercepts t^* . From these intercepts and using Eq. (8) we estimate $D_{\text{H}_2/\text{HDPE}} = 1.58 \times 10^{-6}$ and $1.75 \times 10^{-6} \text{ cm}^2 \text{s}^{-1}$ for the diffusion coefficient of H_2 in HDPE. By comparison, Chang and LaVerne^{5,6} report an average value of $2.2 \times 10^{-6} \text{ cm}^2 \text{s}^{-1}$, as measured during their ^{60}Co irradiation experiments using dynamic outgassing with a sweep gas. Other measurements in the literature range from 1.2×10^{-6} to $5 \times 10^{-6} \text{ cm}^2 \text{s}^{-1}$,^{15,20,21} but it seems likely that Chang and LaVerne's values are most accurate. If this is indeed true, our values of $D_{\text{H}_2/\text{HDPE}}$ are perhaps 25% too small. Considering that diffusion coefficients can be difficult to measure accurately, we consider this to be good agreement.

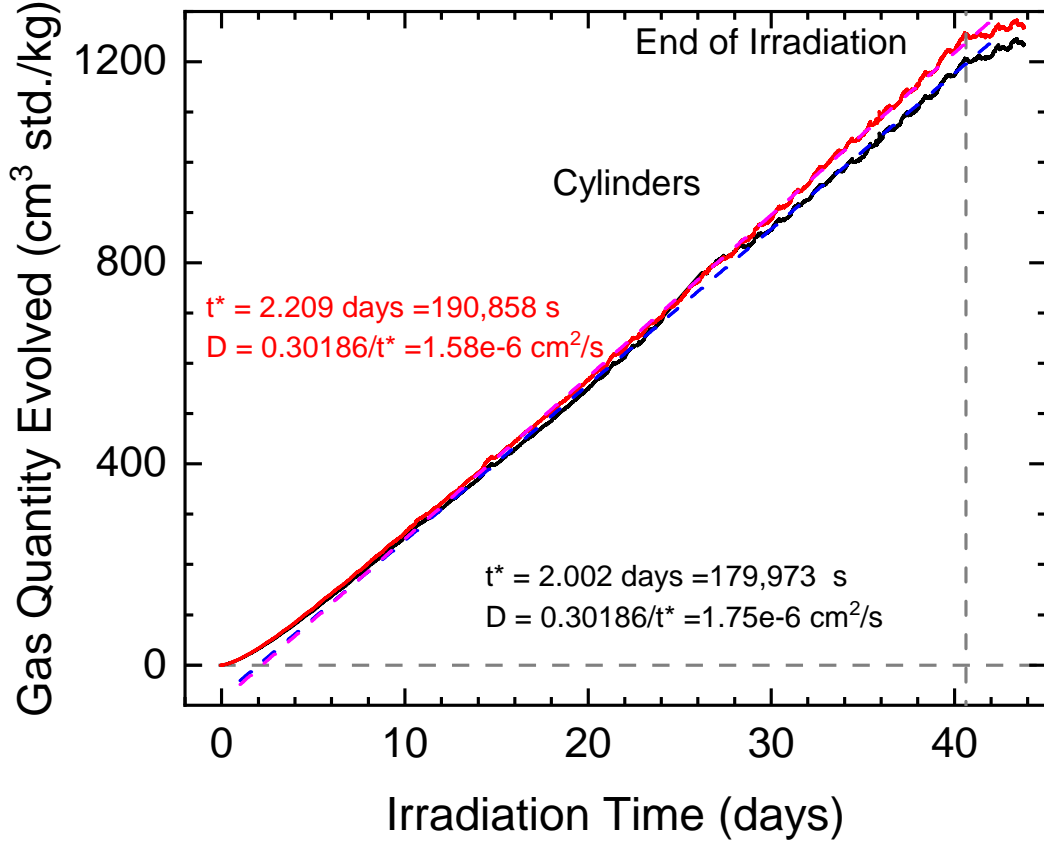


FIG. 6. Irradiation time dependence of the gas quantity evolved from 3.6 cm diameter \times 6.1 cm tall HDPE cylinders during ^{60}Co irradiation to 207 kGy dose at a rate of 5090 Gy day⁻¹. Solid curves show experimental outgassing traces. Dashed straight lines are fitted to both traces for irradiation times of 10 to 40 days, where steady-state outgassing behavior is established. Based on the x-intercept of these lines, we have estimated the diffusion coefficient of H₂ in HDPE.

V. SUMMARY/CONCLUSION

We have irradiated HDPE ribbons and cylinders to ~ 200 kGy dose at 5,090 Gy day⁻¹ using γ -rays from a ^{60}Co source (1.173 and 1.332 MeV primary photon energies). The initial purpose of these experiments was twofold: (1) To evaluate the accuracy of the gas accumulation measurement technique, as implemented at LANL; and (2) To measure the evolved gas composition. Regarding the composition, we found that the evolved gas was mainly (i.e., ~ 98 mol%) H₂, in agreement with previous literature reports. Regarding the technique accuracy, we assessed this by measuring the time- and dose-dependence of the

radiation-chemical evolved gas yield $G_{evolved}$, and compared our results to those measured in the literature using both dynamic outgassing and static gas accumulation methods. For HDPE ribbons with high specific surface area ($\sim 100 \text{ cm}^2 \text{ g}^{-1}$), we measure a dose- and time-invariant value of $G_{evolved} \approx 0.0076 \text{ cm}^3 \text{ std. H}_2 \text{ J}^{-1}$. This is in good agreement with the 0.007 to 0.0077 $\text{cm}^3 \text{ std. H}_2 \text{ J}^{-1}$ range of values reported in the literature for powders, films, and sheets having comparably high specific surface areas, and measured using both dynamic and static accumulation techniques. This favorable comparison suggests that the gas accumulation method, as implemented at LANL, produces accurate values of $G_{evolved}$.

For HDPE cylinders with low specific surface area ($\sim 1.53 \text{ cm}^2 \text{ g}^{-1}$), we find that $G_{evolved}$ increases throughout the irradiation, achieving a value of $\approx 0.0059 \text{ cm}^3 \text{ std. H}_2 \text{ J}^{-1}$ by the conclusion of the experiment but continuing to trend upward. The contrasting time (dose) dependences of $G_{evolved}$ for ribbons and cylinders reflects the interplay of diffusion of radiolytically-generated H_2 in the HDPE, sample dimensions and geometry, and the experimental timescale. To reliably measure $G_{evolved}$, the experimental timescale must be sufficiently long that most of the H_2 can escape. As the specific surface area of the HDPE specimen decreases, a longer timescale is required, and evidently for our cylinders the gas cannot completely escape during the 40-day period of active irradiation.

We used this incomplete escape of radiolytically-generated H_2 to estimate the diffusion coefficient of H_2 in HDPE. Specifically, we developed a model for the generation and two-dimensional diffusion of gas in finite-sized cylinders, and then used this model to analyze our data. In this way, we estimated $D_{\text{H}_2/\text{HDPE}} \approx 1.65 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, which agrees well with measurements in the literature.

Finally, we note that the present measurements, as well as those reported in the literature, are not necessarily relevant to applications of interest to LANL. There are two reasons for this. First, all of these irradiations were performed using ^{60}Co sources, which emit primarily 1.173 and 1.332 MeV photons. The radiation chemistry induced by these high-energy photons may not be representative of the chemistry induced by lower-energy sources, for example 662 keV photons from ^{137}Cs or 59.6 keV photons from ^{241}Am . Different chemical responses could be driven by changes in the primary mechanism(s) of photon/matter interactions at the different energies, e.g., photoelectric effect (dominant at low energies) vs. Compton scattering vs. pair production (dominant at high energies). The second reason is that the dose rates used in the present work, and in literature studies, were 6-8 orders of

magnitude larger than the $\sim 1\text{-}100\text{ Gy year}^{-1}$ rates that are more relevant to LANL applications. The possible issue here is that G_{evolved} might depend on the dose rate. Indeed, our measurements on other materials that are of interest to LANL show that G_{evolved} increases significantly with decreasing dose rate. This observation was not completely surprising, considering that it is predicted by simple kinetic models of radiation-induced radical reaction networks. Additional studies are required to assess both the photon energy and the dose rate dependence of G_{evolved} in HDPE.

-
- [1] T. F. Williams and M. Dole, *J. Am. Chem. Soc.* **81**, 2919 (1958).
 - [2] F. Cracco, A. J. Arvia, and M. Dole, *J. Chem. Phys.* **37**, 2449 (1962).
 - [3] T. Kimura, T. Miyazaki, K. Fueki, and Z. ichiro Kuri, *Bull. Chem. Soc. Jpn.* **41**, 2861 (1968).
 - [4] T. Kimura, K. Fueki, and Z. ichiro Kuri, *Bull. Chem. Soc. Jpn.* **43**, 1657 (1970).
 - [5] Z. Chang and J. A. LaVerne, *J. Phys. Chem. B* **103**, 8267 (1999).
 - [6] Z. Chang and J. A. LaVerne, *J. Poly. Sci. B Polymer Phys.* **39** (2001).
 - [7] Z. Chang and J. A. LaVerne, *J. Phys. Chem. B* **106**, 508 (2002).
 - [8] E. J. Lawton, J. S. Balwit, and R. S. Powell, *J. Poly. Sci.* **32**, 257 (1958).
 - [9] H. Mitsui and F. Hosoi, *Polym. J.* **4**, 79 (1973).
 - [10] H. Mitsui and Y. Shimizu, *J. Polym. Sci., Polym. Chem. Ed.* **17**, 2805 (1979).
 - [11] K. Arakawa, T. Seguchi, Y. Watanabe, and N. Hayakawa, *J Poly. Sci., Polym. Chem. Ed.* **20**, 2681 (1982).
 - [12] Z. Chang and J. A. LaVerne, *Rad. Phys. and Chem.* **62**, 19 (2001).
 - [13] S. B. Dhiman and J. A. LaVerne, *J. Nucl. Mat.* **436**, 8 (2013).
 - [14] M. Dole, D. C. Milner, and T. F. Williams, *J. Am. Chem. Soc.* **80**, 1580 (1958).
 - [15] N. N. Alekseenko, P. V. Volobuev, and S. B. Trubin, *Sov. At. Energy* **53**, 734 (1982).
 - [16] R. R. Barth, K. L. Simmons, and C. S. Marchi, *Polymers for Hydrogen Infrastructure and Vehicle Fuel Systems: Applications, Properties, and Gap Analysis*, Tech. Rep. SAND2013-8904 (Sandia National Laboratories, 2013).
 - [17] J. W. T. Spinks and R. J. Woods, *An Introduction to Radiation Chemistry*, 3rd ed. (John Wiley and Sons, 1990).
 - [18] J. Crank, *The Mathematics of Diffusion*, 2nd ed. (Oxford University Press, 1975).

- [19] H. S. Carslaw and J. C. Jaeger, *Conduction of Heat in Solids*, 2nd ed. (Oxford University Press, 1959).
- [20] T. M. Deas, H. H. Hofer, and M. Dole, *Macromolecules* **5**, 223 (1972).
- [21] R. Ash, R. M. Barrer, and D. G. Palmer, *Polymer* **11**, 421 (1970).